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13. ABSTRACT (Maximum 200 words) Two series of new electroactive and photoactive coil-rod-coil and rod-coil-rod triblock copolymers, poly (pentadecamethylene carboxyester)- <i>block</i> -poly(<i>p</i> -phenylene benzobisthiazole)- <i>block</i> -poly (pentadecamethylene carboxyester) (1), and poly (2,6-benzoxazole)- <i>block</i> - poly(benzobisthiazole decamethylene)- <i>block</i> -poly(2,6-benzoxazole) (2), were synthesized, characterized, and used to investigate the self-assembly properties of rod-coil block copolymers. The progressive band narrowing of the absorption spectrum of thin films of 1 confirmed the effects of spatial confinement with increasing coil block size. Photoluminescence studies of thin films of 1 and 2 showed the effects of self-organization, annealing at 110°C, block lengths, and composition on photophysical properties. Bilayer photoreceptors consisting of a layer of block copolymer as the charge generation layer and a layer of tris(<i>p</i> -tolyl)amine dispersed in polycarbonate as a trap-free hole transport layer were observed to have high quantum efficiency, good photosensitivity and good dark decay.				
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Electroactive and Photoactive Rod-Coil Block Copolymers:
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ELECTROACTIVE AND PHOTOACTIVE ROD-COIL BLOCK COPOLYMERS: SELF-ORGANIZATION AND PHOTOPHYSICAL PROPERTIES

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ABSTRACT

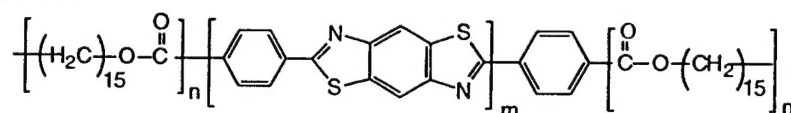
Two series of new electroactive and photoactive coil-rod-coil and rod-coil-rod triblock copolymers, poly (pentadecamethylene carboxester)-*block* - poly(*p*-phenylene benzobisthiazole) - *block* - poly (pentadecamethylene carboxester) (1), and poly(2,6-benzoxazole)-*block*-poly(benzobisthiazole decamethylene)-*block*-poly(2,6-benzoxazole) (2), were synthesized, characterized, and used to investigate the self-assembly properties of rod-coil block copolymers. The progressive band narrowing of the absorption spectrum of thin films of 1 confirmed the effects of spatial confinement with increasing coil block size. Photoluminescence studies of thin films of 1 and 2 showed the effects of self-organization, annealing at 110 °C, block lengths, and composition on photophysical properties. Bilayer photoreceptors consisting of a layer of block copolymer as the charge generation layer and a layer of tris(*p*-tolyl)amine dispersed in polycarbonate as a trap-free hole transport layer were observed to have high quantum efficiency, good photosensitivity and good dark decay.

INTRODUCTION

Rod-coil block copolymers are currently of theoretical [1-4] and experimental [5-7] interest because of their complex morphologies and phase behavior. Because of the thermodynamic incompatibility of the two vastly different conformations of rigid-rod and coil-like blocks and the constraint imposed by the chemical bonding between the blocks, rod-coil block copolymers exhibit a wide range of microphase-separated morphologies. The rich variety of ordered morphologies in this class of block copolymers are being explored and the factors determining their phase behavior are being defined [1-7]. However, rod-coil block copolymers which have been studied so far are non-electroactive and non-photoactive[5-7], thus limiting both the scope of the techniques suitable for investigating the morphologies and applications of the resulting nanophase materials.

In this paper, two series of new electroactive and photoactive rod-coil-rod and coil-rod-coil triblock copolymers: poly (pentadecamethylene carboxester)-*block* - poly(*p*-phenylene benzobisthiazole) - *block* - poly (pentadecamethylene carboxester) (1, CRCA), and poly(2,6-benzoxazole)-*block*-poly(benzobisthiazole decamethylene)-*block*-poly(2,6-benzoxazole) (2, RCRA-1) have been synthesized, characterized, and used to explore the self-assembly properties of block copolymers and the effects of the morphologies of the resulting self-organized nanostructured materials on their solid-state photophysical properties. The chemical structures of the triblock copolymers we investigated are shown below. The poly(*p*-phenylene benzobisthiazole) (3, PBZT) homopolymer, is a well-known conjugated rigid-rod polymer which has interesting photoconductive [8] and light emitting [9] properties. The coil-like blocks of 1 consist of blocks of various lengths of the nonphotoactive and nonelectroactive polyester 4. The poly(2,6-benzoxazole) (5, 2,6-PBO) homopolymer is a conjugated polymer with high modulus and thermal stability [10], that also exhibits liquid crystalline ordered phases in solution [11]. However, its electroactive and photoactive properties have not been reported before. The poly(benzobisthiazole decamethylene) (6, PBTC10) is a non-photoactive and non-electroactive polymer, soluble in common organic solvent such as THF, chloroform. Various techniques, such as

differential scanning calorimetry, polarized optical microscopy, optical absorption and photoluminescence spectroscopies, and cyclic voltammetry, were used to probe and elucidate the morphologies and properties of the block copolymers. Absorption and photoluminescence measurements on the thin films were performed, and confirmed the self-organization of the rigid-coil block copolymers.

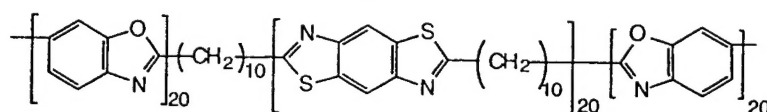


1, CRCA

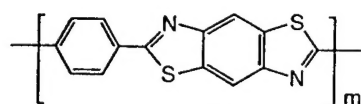
1a : m=9, n=2; 1d: m=9, n=9

1b: m=9, n=3; 1e: m=9, n=19

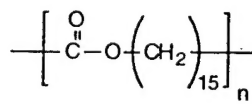
1c: m=9, n=4



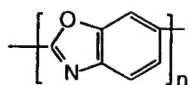
2, RCRA-1



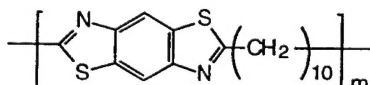
3, PBZT



4, Polyester



5, 2,6-PBO



6, PBTC10

Figure 1. Chemical structures of 1 and 2 copolymers and their related homopolymers.

EXPERIMENTS

The coil-rod-coil triblock copolymers 1a-1e were synthesized by copolymerization of a carboxylic acid-terminated PBZT (HOOC-PBZT-COOH) [11] with the AB-type monomer 16-hydroxyhexadecanoic acid (16-HA). The resulting products of copolymerization were purified by extensive extraction with refluxing acetone, which is a selective solvent for the polyester. Triblock copolymer 2, was synthesized according to modified literature method [11]. In short, carboxylic acid-terminated flexible poly(benzobisthiazole decamethylene) (PBTC10) block (HOOC-B_m-COOH) was synthesized by reacting 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) with excess 1,10-decanedicarboxylic acid in polyphosphoric acid (PPA). Then, 4-amino-3-hydroxybenzoic acid (A) was added to generate the rigid-rod blocks. The rod-coil-rod triblock sample we investigated here is A₂₀B₂₀A₂₀, with average numbers of repeat units of 20 for 2,6-PBO and PBTC10 repeat unit respectively.

Optical quality thin films of 1, 2, and their blends with PMMA were obtained by spin coating onto silica substrates from nitrobenzene(NB)/GaCl₃ solution. The films were then regenerated in methanol and dried in a vacuum oven. The bilayer receptors for the photodischarge measurements were prepared by spin coating the solution of a copolymer onto poly(ethylene terephthalate) (PET) substrates, which were pre-coated with nickel. The copolymer films were then coated with a 20-mm tris(*p*-tolyl)amine/polycarbonate (TTA:PC 40/60, w/w) layer. Photophysical measurements, such as, UV-Vis, steady-state photoluminescence(PL), and charge photogeneration, were all performed on thin films at room temperature. Details of instruments and methods have been previously reported [8,9].

RESULTS AND DISCUSSION

The structures and compositions of the triblock copolymers **1a-1e** and **2** were established by various techniques, including ^1H NMR, ^{13}C NMR, FTIR, DSC, TGA, UV-Vis, and photoluminescence spectroscopies. The expected microphase separation or self-assembly processes of rod-coil triblock copolymers are illustrated in Figure 2. In isotropic solution, the triblock copolymers are in a disorder state. In the solid state, however, phase-separated ordered structures in which the rodlike blocks aggregate into anisotropic domains are the thermodynamically stable structures [1-7]. Thus, the self-assembly process is a kinetic process that occurs during the coagulation of solutions into solids as well as during subsequent processing (e.g. annealing) of the solids. Because the rodlike blocks are electroactive and photoactive, optical techniques can be used as powerful probes of the self-assembly process and the resulting nanostructures.

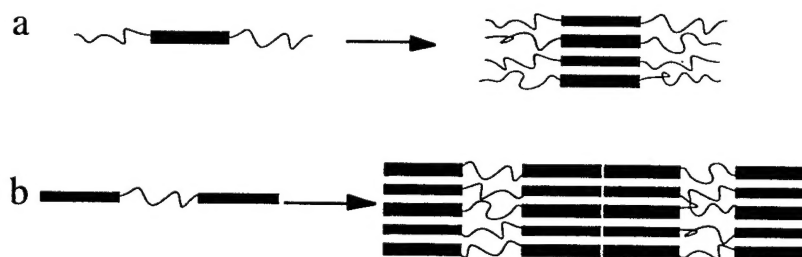


Figure 2. Schematic illustration of self-assembled structures from coil-rod-coil and rod-coil-rod triblock copolymers.

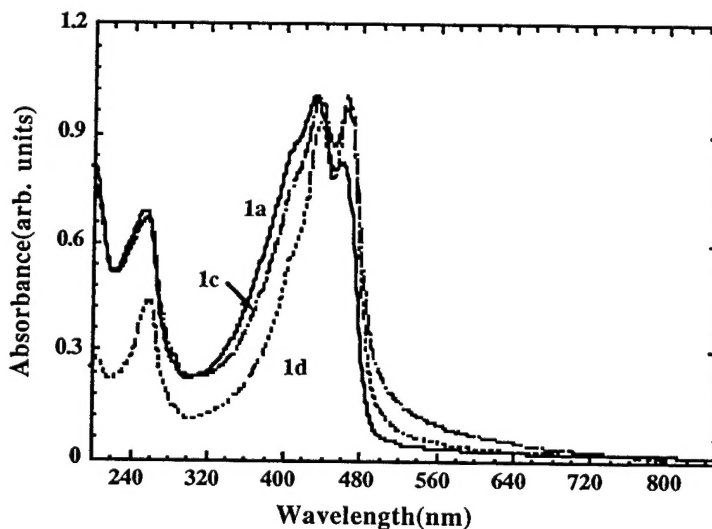


Figure 3. Absorption spectra of thin films of **1a**, **1c** and **1d**.

Figure 3 shows the optical absorption spectra of **1a**, **1c**, and **1d** films cast from nitrobenzene/ AlCl_3 . The absorption bands of the triblock copolymers **1a-1e** have identical maxima at about 438 and 468 nm and a π - π^* absorption edge of 500 nm (2.48 eV). These triblocks with average 9 repeat units of PBZT have essentially identical electronic absorption spectra as the high molecular weight homopolymer ($\text{DP}_n \sim 150$) [9]. However, a novel feature of the UV-Vis spectra of the triblocks is the narrowing of the bandwidth of the main absorption band as the polyester block length increases (**1a** to **1d** in Figure 3). The origin of these effects is the increasing chromophore confinement as the coil-like block length increases.

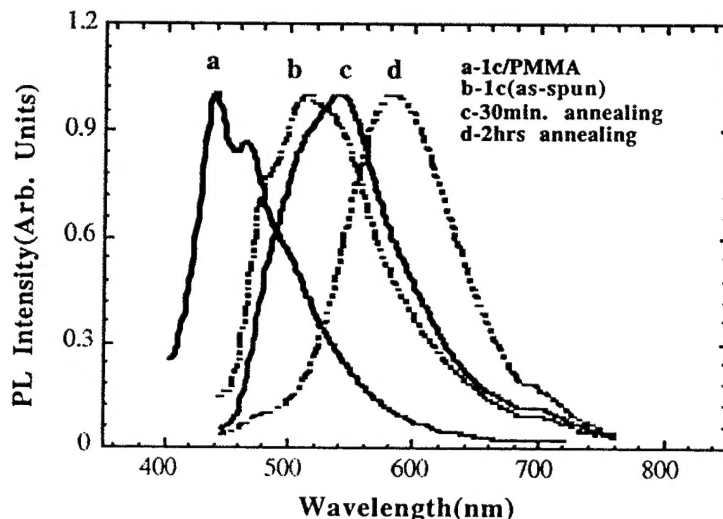


Figure 4. PL spectra of thin films of **1c**: (a) **1c** in PMMA (0.1 wt%); (b) as-spun; (c) annealed at 110 °C for 30 min.; (d) annealed at 110 °C for 2 hours.

Figure 4 show the PL spectra of thin films of **1c**. The PL spectrum of the as-spun film shows a slightly structured emission band with peak at 513 nm and a shoulder peak at 480 nm (Fig. 4b). When the film was annealed at 110 °C for 30 min, the emission band is red-shifted and the PL λ_{max} increase to 540 nm (Fig. 4c). A longer annealing time (2 hours) gave rise to a broad, featureless emission band centered at 583nm and a large Stokes shift (115 nm) (Fig. 4d). For comparison, the emission spectrum of **1c** dispersed in inert PMMA matrix (0.1 wt%) is also shown (Fig. 4a). The PL spectrum of **1c**/PMMA blend shows a well-resolved vibronic structure with peak at 440 nm and a shoulder peak at 465 nm, which is assigned to the single-chain emission of isolated PBZT blocks. Because the broad and structureless emission of conjugated polymers originate chromophore aggregation and excimer formation [9], the PL results of copolymer **1c** not only reflect and evidence three degrees of chromophore aggregation (b,c,d) during the self-assembly process of the same triblock, but also suggest that the self-assembly process is a kinetic one.

The UV absorption spectrum of a thin film of **2** is shown in Figure 5 (curve a). The absorption spectrum of **2** is simply the superposition of those of the two corresponding homopolymers, showing peaks at 364, 380, 404 and 431 nm, and a π - π^* transition band edge of 2.73 eV. Figure 5 also shows the PL emission spectra of thin films of 2,6-PBO homopolymer (Fig. 5d), copolymer **2** as a pure film (Fig. 5c) and as a blend in PMMA (0.1wt%, curve 5b). The thin films were all excited at 360 nm, where the absorption band of the 2,6-PBO is located. The emission spectrum of **2** shows a broad, featureless emission band with λ_{max} at 510 nm, and a significant Stokes shift. By dispersing the triblock in PMMA, the emission showed a well-resolved vibronic structure with peaks at 433, 460 and 490 nm and a very small Stokes shift (2 nm). The spectrum of 2,6-PBO shows a broad, featureless emission band centered at 560 nm (Fig. 5d), which is characteristic of the excimer aggregate emission [9]. The PL spectra evolution was also accompanied by quantum efficiency enhancement. More than 15-fold enhancement of PL quantum efficiency was observed, being 1% for 2,6-PBO, 3% for **2**, and 15% for 2/PMMA blend (0.1wt%). The large blue shift of the PL spectrum of 2/PMMA (Fig. 5b), together with the dependence of PL quantum efficiency on concentration suggest that the broad and featureless emission of **2** (Fig. 5c) is from the aggregation of the 2,6-PBO blocks, which leads to the

formation of excimer, a phenomenon which severely quenches the PL quantum efficiency [9]. Because the emission peak of the copolymer is 50 nm blue-shifted compared to that of the homopolymer, one can infer that the domains of 2,6-PBO blocks are much smaller than those of the homopolymer. The PL studies indicate that for 2, microphase separation does occur in the solid state and that the resulting aggregates have strong effects on photophysical properties.

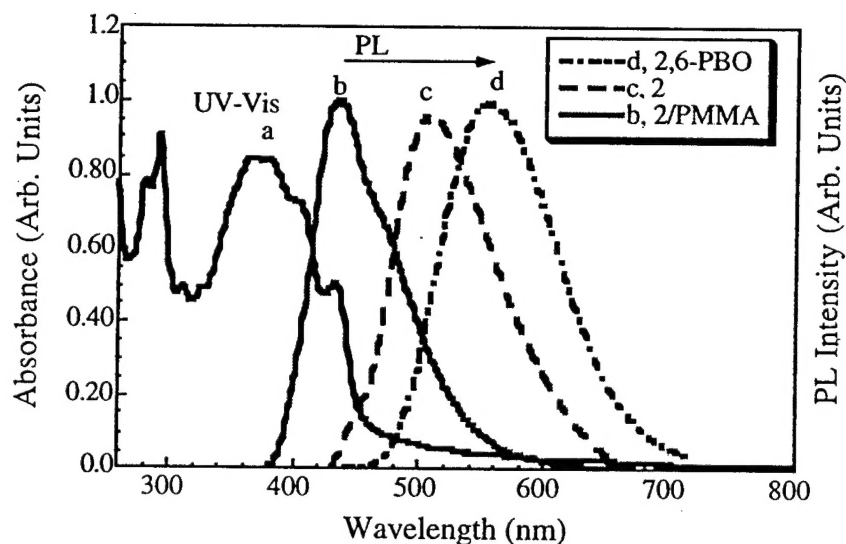


Figure 5. Optical absorption spectrum of 2 (a) and PL emission spectra of thin films excited at 360 nm: (b) 2/PMMA(0.1wt%), (c) 2, and (d) 2,6-PBO.

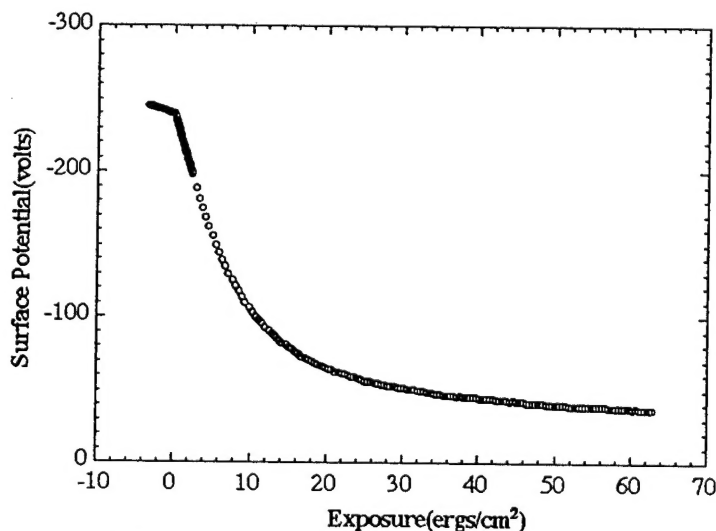


Figure 6. Photoinduced discharge curve for 1d /TTA bilayer device. The excitation wavelength is 470 nm.

Figure 6 shows the photoinduced discharge curve for the 1d /TTA bilayer device (80 nm thickness of 1d) which was initially charged to a surface potential of ~ 250 V. Three important device parameters: photosensitivity, dark decay and residual potential can be obtained from Figure 6. For the 1d/TTA bilayer device, photosensitivity of ~ 8 ergs/cm², dark decay of ~ 4 V/cm, and residual potential of ~ 30 V were obtained. At high electric field ($\sim 8 \times 10^5$ V/cm), photogeneration quantum efficiency as high as 28% was achieved. Compared to PBZT/TTA bilayer device which

has a photosensitivity of 12 ergs/cm² and a quantum efficiency of ~25% at a field of 8×10^5 V/cm [8], **1d** /TTA device has a similar quantum efficiency but a better photosensitivity. The superior performance of block copolymers as charge photogeneration layers is not currently understood but will be further investigated.

CONCLUSION

Two new series of electroactive and photoactive rod-coil triblock copolymers have been synthesized, characterized and their self-assembly properties exploited to construct nanostructured materials. Our photophysical studies demonstrate the aggregation of the rigid-rod blocks and the effects of self-organization, annealing at 110 °C, block lengths, and composition on photophysical properties. Bilayer photoreceptors using **1d** as the charge generation layer exhibit high quantum efficiency (> 28 % at $\sim 10^6$ V/cm), good photosensitivity (8 ergs/cm²) and good dark decay (< 5 V/s). These results suggest that rod-coil block copolymers with conjugated rodlike blocks are promising building blocks for preparing functional, electroactive and photoactive nanostructured polymer systems.

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